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**REMARKS**

The Office Action of April 24, 2001 has been received and carefully reviewed. It is submitted that, by this Amendment, all bases of rejection and objection are traversed and overcome. Upon entry of this Amendment, Claims 1-25 and 27-32 remain in the application. New claims 33-65 have been added in order to set forth specific additional embodiments of Applicants' invention.

Claims 1-7 and 10-14 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Ogawa et al. (6,042,797) in view of "New Sorbents for Olefin/paraffin separations by adsorption..." Ralph T. Yang and E.E. Kikkinides, AIChE Journal, March 1995, Vol. 41, No. 3, pp. 509-517. (Yang)

The Examiner states that Ogawa discloses a process for removing ethylene from a gas mixture containing ethylene and a sulfur compound (e.g., sulfur oxide) by contacting the gas mixture with an adsorbent which comprises a silver compound (silver nitrate) and zeolite. The Examiner recognizes that Ogawa does not specifically disclose that the carrier comprises a monolayer of a silver compound on the adsorbent surface. However, he stated that it is optional that only silver compound is impregnated on the adsorbent (Applicants do not see this in Ogawa). Therefore, the Examiner concluded that this limitation is embraced by the reference (Applicants respectfully take issue with this conclusion). The Examiner also recognized that the reference does not disclose that the retaining of the alkene is accomplished by formation of  $\pi$ -complexation bonds. However, it is known that the bonds between the silver compound and alkene occur by  $\pi$ -complexation bonds (See col. 2, line 59 through col. 8, line 7) (Applicants also take issue with this statement--the cite from Ogawa is not discussing  $\pi$ -complexation).

The Examiner notes that Ogawa does not disclose that silver compound is dispersed on the adsorbent, does not disclose the silver compound is silver halide and the carrier is silica which has a surface area between 50 to 2,000 m<sup>2</sup>/g.

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The Examiner states that Yang 1995 discloses a process for separating ethylene/propylene from a paraffinic feed. The Examiner erroneously asserts that the Yang 1995 adsorbent comprises a silica support and silver salt (e.g.,  $\text{AgNO}_3$ ,  $\text{AgCl}$ ).

In contrast, Applicants submit that the 1995 reference actually discloses the use of  $\text{AgNO}_3$  to prepare either 1) silver exchanged zeolites; or 2) silver exchanged resins; however, nowhere in the reference is silver taught or suggested for use with a silica support. The reference then teaches 3) monolayer dispersion of  $\text{CuCl}$  on alumina. Silica is not disclosed in the Yang 1995 reference.

The Examiner concluded that it would have been obvious to one having ordinary skill in the art at the time the invention was made to have modified the Ogawa process by dispersing the silver compound on the carrier as taught by Yang (as stated above, Applicants take issue with this interpretation of Yang 1995) because Yang discloses that it is effective to remove alkene when using an adsorbent wherein a silver compound is dispersed on the adsorbent.

Claims 8 and 9 stand rejected under 35 U.S.C. 103(a) as being unpatentable over the references as applied to claims 1-7 and 10-14 above, and further in view of Ramachandran et al. (5,744,687).

Claims 26-28 stand rejected under 35 U.S.C. 103(b) as being unpatentable over Milton (2,882,243).

The Examiner stated that it would have been obvious to one having ordinary skill in the art at the time the invention was made to have modified the Milton process by utilizing a feedstock containing a tiny amount of hydrogen sulfide (e.g., 0.01 ppm) because it would be expected that the tiny amount of hydrogen sulfide present in the feedstock of Milton would not affect the outcome of the process of Milton.

Applicants do not acquiesce to the Examiner's conclusion, as it begs the issue, and is also not practical. As stated in Applicants' application at page 3, lines 5-10:

[I]n catalytic reforming, the catalyst used is often platinum supported on high-purity alumina. However, the platinum on the

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catalyst is seriously deactivated by sulfur compounds, and therefore the feedstock is desulfurized to less than 3 ppm by weight of sulfur before the reforming.

In order to preserve the expensive platinum in a catalytic reforming process, the desulfurization is taken substantially to the limits—in other processes, one would generally not see feedstocks having as low as 3 ppm hydrogen sulfide. As such, it would be extremely expensive and time consuming, if not impossible, to desulfurize feedstock to a level of "0.01 ppm" as suggested by the Examiner.

#### Discussion

Applicants' invention as defined in claims 1, 11, 15 and 26 is predicated on the fact that it is not necessary to desulfurize to extremely low levels:

[T]his novel adsorbent fortuitously and unexpectedly substantially maintains its adsorbent capacity and preference for the alkene in the presence of the sulfur compound. This is highly desirable, as this sulfur tolerant and/or resistant adsorbent (as well as the other novel adsorbents described hereinbelow) obviates step(s) conventionally necessary to desulfurize the cracked gas stream(s). (emphasis added) page 10, lines 28-36

The Examiner is further directed to the instant application at page 13, lines 13-22:

The novel adsorbents were exposed to very severe amounts, for example the hydrogen sulfide was present in amounts up to about 66 mole%. In sharp contrast, a conventional cracked gas stream before any desulfurizing distillation steps contains hydrogen sulfide present in amounts of about 0.01 mole% [100 ppm]. As such, the data presented hereinbelow indicate that the novel adsorbents of the present invention would be quite robust, ie. very tolerant and/or resistant to H<sub>2</sub>S under normal operating conditions. (emphasis added)

Applicants have amended independent claims 1 and 11 to replace "sulfur compound" with "hydrogen sulfide." It is submitted that this removes Ogawa as a primary reference. Ogawa states at Col. 6, lines 24 et seq.:

Specifically, [the gas] may be a gas containing ethylene, for example, the atmosphere, an exhaust gas, or a gas in a storage chamber of the crops. The adsorbent is effective also in a case where the gas contains not only ethylene but also carbon monoxide, carbon dioxide, hydrogen, oxygen, nitrogen oxide, sulfur oxide. . .

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In Ogawa, the olefins are being removed from the atmosphere or an exhaust gas. Exhaust gas contains by-products of burning: sulfur oxides, carbon oxides, etc. In Applicant's invention as defined in claims 1 and 11, it is recited that the adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of hydrogen sulfide. This is remarkable in that hydrogen sulfide has been recognized as being capable of potentially deactivating entire adsorbents. Thus, hydrogen sulfide has been recognized as reacting detrimentally; whereas sulfur oxide is substantially an inert by-product.

Neither Ogawa nor any of the other cited references disclose adsorbents which substantially maintain their adsorbent capacity and preference for the alkene in the presence of hydrogen sulfide as recited in Applicants' claims 1 and 11. As such, it is submitted that Applicants invention as defined in claims 1 and 11, as well as in all claims dependent therefrom, is not anticipated, taught or rendered obvious by Ogawa or Yang 1995, either alone or in combination, and patentably defines over the art of record.

Applicants do not acquiesce to the Examiner's rejection of claims 26-28. However, in order to expedite prosecution, Applicants have canceled claim 26 and incorporated the subject matter therein into "objected to" claim 32. Claim 27 has been amended to depend from amended claim 32. As such, it is submitted that claims 27, 28 and 32 are in condition for allowance.

The Examiner stated that claims 15-25 are allowed; and that claims 29-32 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. It is submitted that, in fact, claim 31 was dependent upon allowed claim 15, and therefore Applicants have not rewritten claim 31. However, claims 29 and 30 (as well as 32, as mentioned above) have been so rewritten.

In the Examiner's statement of reasons for the indication of allowable subject matter, he stated that "essentially all" cationic sites of the ion-exchanged zeolite contain silver cation or copper cation "as called for in claim 15". However, Applicants call the Examiner's attention to claim 15 as originally

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filed (and as it remains), which recites that "a majority" of the sites have silver cation or copper cation present.

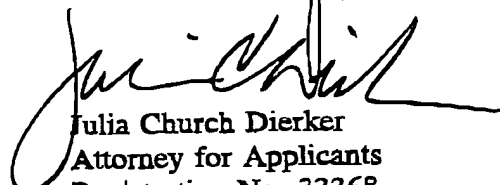
Support for the amendment to page 11, lines 1-17 may be found in U.S. application serial no. 09/179,667 (which had been incorporated by reference into the subject application) at page 3, line 34 - page 4, line 1 of that application. Support for the amendment to page 11, between lines 20 and 21 may also be found in U.S. application serial no. 09/179,667, at page 16, lines 16-19 of that application.

In summary, Claims 1-25 and 27-32 remain in the application. Claim 26 has been canceled. New claims 33-65 have been added in order to set forth additional specific embodiments of Applicants' invention. It is submitted that, through this amendment, Applicants' invention as set forth in these claims is now in a condition suitable for allowance.

Further and favorable consideration is requested. If the Examiner believes it would expedite prosecution of the above-identified application, he is cordially invited to contact Applicants' Attorney at the below-listed telephone number.

Respectfully submitted,

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**VERSION OF AMENDMENTS WITH MARKINGS**  
**TO SHOW CHANGES MADE**

**In the specification:**

**At page 1, lines 4-9, please amend the paragraph as follows:**

This application is related to co-pending United States Application Serial No. 09/177,256, filed October 22, 1998, and to United States Application Serial No. 09/179,667, filed October 27, 1998, now U.S. Patent No. 6,215,037, each of which applications is incorporated herein by reference in its entirety.

**Please amend the paragraph at page 11, lines 1-17 as follows:**

In a further embodiment, a novel method is disclosed for separating a diene from a mixture including the diene and a sulfur compound. The process comprises the step of contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component. The adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, with silver cation or copper cation present at some or all of the exchangeable cationic sites. Substantial cation exchange is preferred so that at least half of the cationic sites of the ion exchange zeolite contain a copper or silver cation [and a majority of the sites have silver cation or copper cation present]. In [the more] a preferred embodiment, the majority of the cationic sites of the ion-exchanged zeolite contain silver cation. In an even more preferred embodiment, essentially all cationic sites of the ion-exchanged zeolite contain the silver cation.

**Page 11, between lines 20 and 21, please insert the following paragraph:**

The Cu-zeolites of the invention were prepared by ion exchanging with a solution of CuCl<sub>2</sub> or Cu(NO<sub>3</sub>)<sub>2</sub>, followed by reduction of Cu<sup>+2</sup> to Cu<sup>+1</sup>.

**In the claims:**

1. (Amended) A method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a

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gaseous mixture including the alkene and [a sulfur compound] hydrogen sulfide, the method comprising the steps of:

contacting the gaseous mixture with an adsorbent which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-adsorbed component and an alkene-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having a monolayer of a silver compound dispersed on substantially the entire surface area, the silver compound releasably retaining the alkene; and the carrier comprising a plurality of pores having a pore size greater than the effective molecular diameter of the alkene; and

changing at least one of the pressure and temperature to thereby release the alkene-rich component from the adsorbent;

wherein the adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of the [sulfur compound] hydrogen sulfide.

11. (Amended) A sulfur tolerant adsorbent for preferential adsorption of gaseous alkene from a gaseous mixture including the alkene and [a sulfur compound] hydrogen sulfide, the adsorbent comprising:

a carrier; and

a silver compound supported on the carrier, wherein the silver compound is a silver salt, and wherein the salt is selected from the group consisting of acetate, benzoate, bromate, chlorate, perchlorate, chlorite, citrate, fluoride, nitrate, nitrite, and sulfate;

[wherein the carrier has a BET surface area greater than about 50 square meters per gram and up to about 2,000 square meters per gram and comprising a plurality of pores having a pore size greater than about 3 angstroms and up to about 10 microns;]

and wherein the adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of the [sulfur compound] hydrogen sulfide.

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15. (Amended) A method for separating a diene from a mixture including the diene and a sulfur compound, the method [process] comprising the step of:

contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and a majority of the sites having silver cation or copper cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation, and further wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the sulfur compound.

Please cancel claim 26 without prejudice.

27. (Amended) The method as defined in claim [26] 32 wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof.

28. (Amended) The method [process] as defined in claim 27 wherein a selected pressure of preferential adsorption is a first pressure, and a pressure of release is a second pressure less than the first pressure, wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres.

29. (Amended) A method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture including the alkene and a sulfur compound, the method comprising the steps of:



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contacting the gaseous mixture with an adsorbent which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-adsorbed component and an alkene-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having a monolayer of a silver compound dispersed on substantially the entire surface area, the silver compound releasably retaining the alkene; and the carrier comprising a plurality of pores having a pore size greater than the effective molecular diameter of the alkene; and

changing at least one of the pressure and temperature to thereby release the alkene-rich component from the adsorbent;

wherein the adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of the sulfur compound, [The method as defined in claim 1] wherein the sulfur compound is hydrogen sulfide, and wherein the hydrogen sulfide is present in amounts up to about 66 mole%.

30. (Amended) A sulfur tolerant adsorbent for preferential adsorption of gaseous alkene from a gaseous mixture including the alkene and a sulfur compound, the adsorbent comprising:

a carrier; and

a silver compound supported on the carrier, wherein the silver compound is a silver salt, and wherein the salt is selected from the group consisting of acetate, benzoate, bromate, chlorate, perchlorate, chlorite, citrate, fluoride, nitrate, nitrite, and sulfate;

wherein the carrier has a BET surface area greater than about 50 square meters per gram and up to about 2,000 square meters per gram and comprising a plurality of pores having a pore size greater than about 3 angstroms and up to about 10 microns;

and wherein the adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of the sulfur compound, [The method as defined in claim 11] wherein the sulfur compound is hydrogen

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sulfide, and wherein the hydrogen sulfide is present in amounts up to about 66 mole%.

32. (Amended) A method for separating a diene from a mixture including the diene and a sulfur compound, the method comprising the steps of:  
contacting the mixture with an adsorbent which preferentially adsorbs the diene at a first temperature, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises zeolite A having exchangeable cationic sites, a plurality of the zeolite A sites having an alkali metal cation or an alkaline earth metal cation present; and  
releasing the diene-rich adsorbed component from the adsorbent by elevating the temperature to a second temperature which ranges between about 70°C and about 120°C;

wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the sulfur compound, [The method as defined in claim 26] wherein the sulfur compound is hydrogen sulfide, and wherein the hydrogen sulfide is present in amounts up to about 66 mole%.

Please add the following new claims:

33. The sulfur tolerant adsorbent as defined in claim 11 wherein the carrier has a BET surface area greater than about 50 square meters per gram and up to about 2,000 square meters per gram and comprising a plurality of pores having a pore size greater than about 3 angstroms and up to about 10 microns.

34. A method for separating a diene from a mixture including the diene and hydrogen sulfide, the method comprising the step of:

contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having

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exchangeable cationic sites, and at least some of the sites having silver cation or copper cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation, and further wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the hydrogen sulfide.

35. The method as defined in claim 34 wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof, and wherein the method further comprises the step of changing at least one of the pressure and temperature to thereby release the diene-rich component from the adsorbent.

36. The method as defined in claim 34 wherein the diene is 1,3-butadiene, and wherein the mixture includes 1,3-butadiene and at least one other  $C_4$  unsaturated compound.

37. The method as defined in claim 34 wherein a majority of the cationic sites of the ion-exchanged zeolite contain the silver cation.

38. The method as defined in claim 34 wherein a majority of the cationic sites of the ion-exchanged zeolite contain the copper cation.

39. The method as defined in claim 34 wherein the mixture comprises at least one mono-olefin having as many carbon atoms as the diene, wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof; and wherein the mono-olefin is selected from the group consisting of butene, hexene, octene, and mixtures thereof.

40. The method as defined in claim 39 wherein the mono-olefin is butene and the diene is butadiene.

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41. The method as defined in claim 39 wherein the mixture comprises the mono-ol fin in a gaseous state and saturated with the diene.

42. The method as defined in claim 34 wherein essentially all cationic sites of the ion-exchanged zeolite contain the silver cation.

43. The method as defined in claim 35 wherein the selected pressure of preferential adsorption is a first pressure, and the pressure of release is a second pressure less than the first pressure, wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres.

44. The method as defined in claim 35 wherein the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than the first temperature, wherein the first temperature is in a range of about 0°C to about 150°C, and wherein the second temperature is in a range of about 70°C to about 250°C.

45. The method as defined in claim 34 wherein the at least some of the sites have silver cation present.

46. The method as defined in claim 34 wherein the at least some of the sites have copper cation present.

47. The method as defined in claim 34 wherein essentially all cationic sites of the ion-exchanged zeolite contain the copper cation.

48. A method for separating a diene from a mixture including the diene and hydrogen sulfide, wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof, wherein the mixture comprises at least one mono-olefin having as many carbon atoms as the

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dien , and wherein the mono-olefin is selected from the group consisting of butene, hexene, octene, and mixtures thereof, the method comprising the steps of:

contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and at least some of the sites having silver cation or copper cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation, and further wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the hydrogen sulfide;

changing at least one of the pressure and temperature to thereby release the diene-rich component from the adsorbent, wherein the selected pressure of preferential adsorption is a first pressure, and the pressure of release is a second pressure less than the first pressure, wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres;

and wherein the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than the first temperature, wherein the first temperature is in a range of about 0°C to about 150°C, and wherein the second temperature is in a range of about 70°C to about 250°C.

49. The method as defined in claim 48 wherein the mono-olefin is butene and the diene is butadiene.

50. The method as defined in claim 48 wherein the mixture comprises the mono-olefin in a gaseous state and saturated with the diene.

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58. The sulfur tolerant adsorbent as defined in claim 55 wherein a majority of the cationic sites of the ion-exchanged zeolite contain the silver cation.

59. The sulfur tolerant adsorbent as defined in claim 55 wherein a majority of the cationic sites of the ion-exchanged zeolite contain the copper cation.

60. The sulfur tolerant adsorbent as defined in claim 55 wherein essentially all cationic sites of the ion-exchanged zeolite contain the silver cation.

61. The method as defined in claim 55 wherein essentially all cationic sites of the ion-exchanged zeolite contain the copper cation.

62. The sulfur tolerant adsorbent as defined in claim 55 wherein the mixture comprises at least one mono-olefin having as many carbon atoms as the diene, wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof; and wherein the mono-olefin is selected from the group consisting of butene, hexene, octene, and mixtures thereof.

63. The sulfur tolerant adsorbent as defined in claim 62 wherein the mono-olefin is butene and the diene is butadiene.

64. The method as defined in claim 55 wherein the hydrogen sulfide is present in amounts up to about 66 mole%.

65. The method as defined in claim 1 wherein the gaseous mixture is contained in a conventional cracked gas stream before any desulfurizing distillation steps.



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